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Enhancement of Reactivity in Surfactant-Modified Sorbents for Sulfur Dioxide Control

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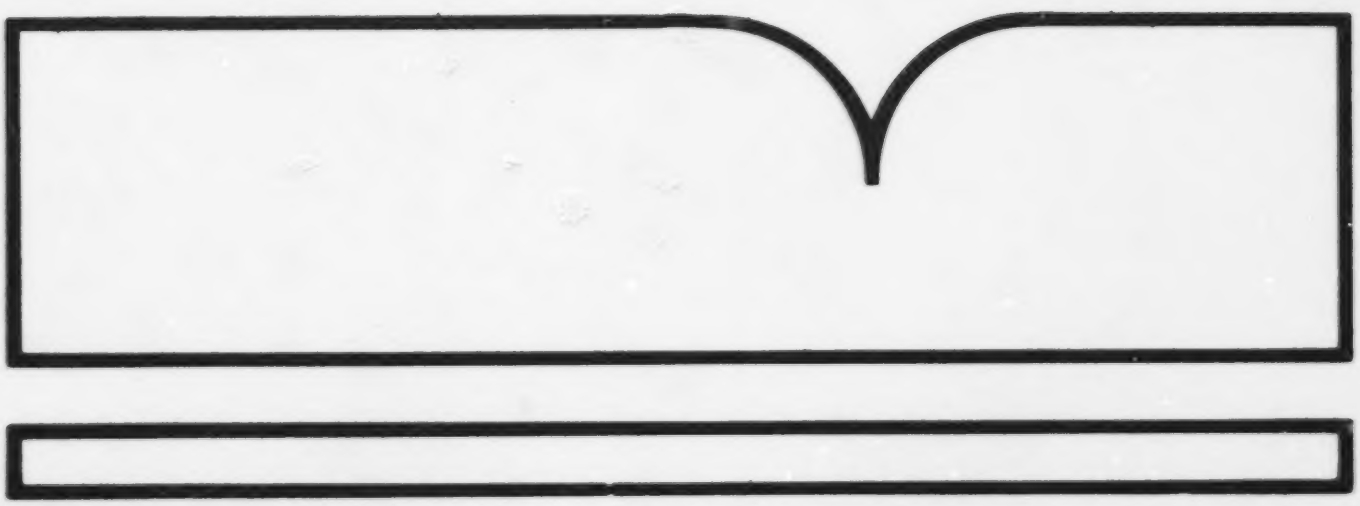

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16. ABSTRACT The paper discusses the enhancement of reactivity in surfactant-modified sorbents for SO2 control. Injecting calcium-based sorbents into the post-flame zone of utility boilers can achieve SO2 captures of 50-60% at a stoichiometry of 2. Calcium hydroxide--Ca(OH)2--appears to be the most effective commercially effective sorbent. Recent attempts to modify Ca(OH)2 by adding calcium lignosulfonate with the water of hydration have succeeded in enhancing its effectiveness. Sulfation experiments in an electrically heated isothermal flow reactor have been used to determine the mechanism of enhancement. Particle size reduction, which in some applications accompanies lignosulfonate addition, does not appear to be required for increased SO2 capture. Similarly, the accelerated rate of dehydration observed in modified hydroxides does not appear to be important. The primary cause of increased reactivity in modified sorbents is the ability of the calcium lignosulfonate to retard the rate of sintering, and thus to retain pore volume and reactive surface area. It was also observed that the presence of SO2 during calcination affects the structure of sorbents favorably, allowing them to retain higher pore volumes than without SO2. This effect may also occur by a slowing of the sintering process, possibly by inhibiting the exchange at pore walls of migrating CaO species with lattice vacancies.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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Sulfur Dioxide	Stationary Sources	07B 07C
Sorbents	Calcium Lignosulfonate	11G
Surfactants		11K
Boilers		13A
Calcium Hydroxides		
Calcium Oxides		
Sulfonation		

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Enhancement of Reactivity in Surfactant-Modified Sorbents for Sulfur Dioxide Control

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Injection of calcium-based sorbents into the postflame zone of utility boilers is capable of achieving sulfur dioxide (SO_2) captures of 50–60% at a stoichiometry of 2. Calcium hydroxide [$Ca(OH)_2$] appears to be the most effective commercially available sorbent. Recent attempts to modify $Ca(OH)_2$ by adding calcium lignosulfonate with the water of hydration have succeeded in enhancing its effectiveness. The particle size reduction, which in some applications accompanies lignosulfonate addition, does not appear to be a prerequisite for increased SO_2 capture. Similarly, the accelerated rate of dehydration observed in modified hydroxides does not appear to be an important mechanism in the enhancement. The primary cause of increased reactivity in modified sorbents is the ability of calcium lignosulfonate to retard the rate of sintering and thus to retain pore volume and reactive surface area.

The injection of calcium-based sorbents into the postflame zone of a boiler for the purpose of controlling SO_2 emissions has been studied extensively. Particular attention has been paid to the most effective sorbent for the process. Limestone ($CaCO_3$), lime (CaO), and hydrated lime [$Ca(OH)_2$], as well as modified forms of the latter two, have been tested. Of the commercially available materials, $Ca(OH)_2$ has been demonstrated consistently to achieve

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the highest levels of SO_2 capture (Overmoe et al., 1985; Beittel et al., 1985; Bortz and Flament, 1985; Slaughter et al., 1985).

Several approaches to enhance the reactivity of commercial sorbents have been tried. Calcination and hydration conditions can be optimized to produce modest increases in the reactivity of hydroxides (Kirchgessner et al., 1986). Chemical additives such as alkali metals have been shown to enhance SO_2 capture in calcium-based sorbents (Borgwardt et al., 1987), but it has also been shown that these volatile promoters are redeposited on the ash particles during coal firing and their effectiveness is lost (Slaughter et al., 1986; Muzio et al., 1986). The most recent work along these lines demonstrates that the surfactant, calcium lignosulfonate, can be added to $Ca(OH)_2$ in the water of hydration to increase its ability to capture SO_2 by as much as 15–20 relative % (Kirchgessner and Lorrain, 1987). Lignosulfonate was originally chosen because it is known to be compatible with calcium-based systems, it is relatively inexpensive, and in some applications, it has dispersant properties. Under current market conditions for calcium hydroxide and calcium lignosulfonate, it has been estimated that increases in SO_2 capture greater than 3–5 relative % will produce an economic benefit.

The first laboratory-scale study of the modified sorbent showed that lignosulfonate addition decreased the mass median particle size of the resulting hydroxide from 12 to 3 μm. The effect of particle size on reactivity is well documented (McCarthy et al., 1986; Borgwardt and Bruce, 1986a; Cole et al., 1986) and is of the order −0.20 to −0.35 (Ishihara et al., 1975; Gullett and Blom, 1987; Gullett and Kramlich, 1987). The enhanced reactivity displayed by this material was, therefore, attributed largely to particle size reduction (Kirchgessner and Lorrain, 1987). Subsequently, however, the modified hydroxide was produced on a commercial scale and tested in combustors ranging from pilot to utility scale. While the modified sorbent in that case showed no significant reduction in particle size, a substantial increase in SO_2 capture was again observed. A recent laboratory study which focused on the structural changes undergone by the modified sorbent during furnace injection showed that it dehydrates (calcines) more quickly and is more resistant to sintering than the unmodified sorbent (Kirchgessner and Jozewicz, 1988). It could be hypothesized that more rapid dehydration would allow the sorbent a longer period of time in its reactive form to react with SO_2. Alternatively, it could be argued that a delay in sintering would allow the sorbent to retain higher specific surface areas and porosities and, therefore, to remain more reactive longer. The relationship of higher calcined surface areas to higher reactivity with SO_2 is well established (Newton et al., 1985; Harrison et al., 1985; Cole et al., 1985; Beittel et al., 1985; Slaughter et al., 1985; Borgwardt and Bruce, 1986b). Borgwardt and Bruce (1986b) have shown reactivity to vary with square of the specific surface area of the calcined sorbent over the range 2–63 m^2/g. The importance of porosity was noted by Hartman et al. (1978), and the role of pore volume distribution was discussed by Ulerich et al. (1978). Larger pores are generally regarded as more favorable, both to avoid pore filling by the sulfation product (Simons, 1988) and to minimize resistance to the diffusing species. Gullett et al. (1988) have even suggested that a combination of surface area in the range 40–50 m^2/g and of porosity around 0.4 could prove to be optimal for SO_2 capture.

The primary purpose of the sulfation experiments discussed in this paper was to clarify the relative roles of particle size reduction, accelerated dehydration rate, and retarded sintering rate in enhancing the SO_2 capture by lignosulfonate-modified $Ca(OH)_2$ sorbents. A secondary focus was to determine the effect of SO_2 on sorbent structure when it is present during calcination and the potential interactive effect of lignosulfonate and SO_2 on sorbent structure and reactivity.

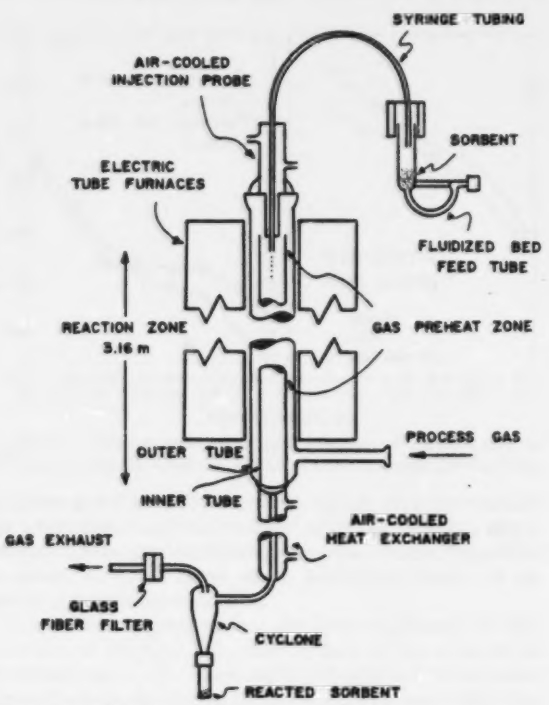

Figure 1. Isothermal flow reactor.

Experimental Section

Materials. The $Ca(OH)_2$ tested in this study was produced from a commercial CaO obtained from the Longview Lime Division of the Dravo Lime Company in Saginaw, AL. The additive used in the modified $Ca(OH)_2$ is calcium lignosulfonate. This material is a partially desugared variety of lignosulfonate available in the form of a water-soluble dry powder from the Georgia Pacific Corporation under the tradename Lignosite.

Hydration. Hydrates are produced in a steam-jacketed Ross ribbon blender. To produce conventional $Ca(OH)_2$, the blender is loaded with 6.8 kg of pulverized CaO and allowed to reach a temperature of 30–50 °C. A total of 3.7 kg of water is then added at a constant rate for 40 min. The blender is run for an additional 20 min while the heat of reaction drives off excess water, leaving a dry $Ca(OH)_2$ product [DH-$Ca(OH)_2$]. The procedure for producing surfactant-modified $Ca(OH)_2$ [SM-$Ca(OH)_2$] is identical except that the 3.7 kg of water contains 102 g of Lignosite. This yields a $Ca(OH)_2$ product containing approximately 1% calcium lignosulfonate, the amount shown by Kirchgessner and Lorrain (1987) to be optimal for enhancement of SO_2 capture.

Reactor. The electrically heated isothermal flow reactor into which the hydrates are injected is shown in Figure 1. The reaction chamber consists of two concentric 3.35-m-long quartz tubes heated by three Lindberg tube furnaces. The inner tube has a 18-mm i.d., and the outer tube has a 50.8-mm o.d. Premixed gases enter the reactor at the bottom of the annulus between the inner and outer tubes and are heated as they move upward. At the top of the

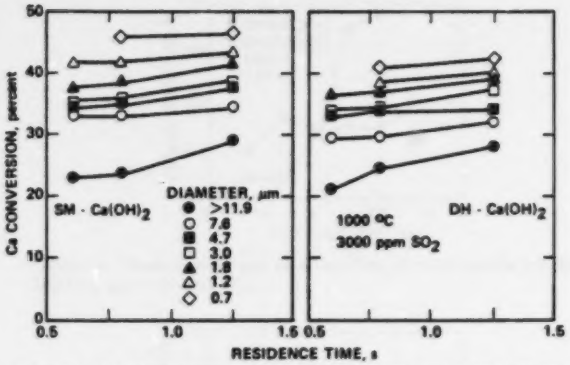

Figure 2. Calcium conversion for SM-$Ca(OH)_2$ and DH-$Ca(OH)_2$ as a function of residence time and particle size.

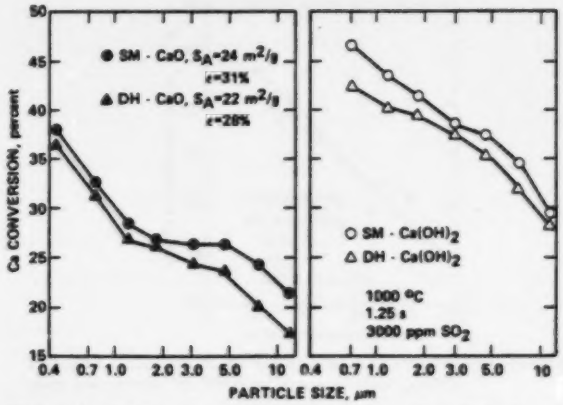

Figure 3. Calcium conversion as a function of particle size for SM-CaO versus DH-CaO and for SM-$Ca(OH)_2$ versus DH-$Ca(OH)_2$.

reactor they enter the inner tube with the sorbent and move downward through the reaction zone. Gases and solids exit the reactor through an air-cooled heat exchanger which quenches the reactant stream to approximately 280 °C. Solids are captured in a cyclone followed by a glass fiber filter. Sorbent is fed from a fluidized bed feed tube through 1.19-mm-i.d. syringe tubing. The reactor is operated at nominal temperatures of 700–1000 °C and nominal residence times of 0.6–1.5 s. Residence time is adjusted by varying gas flow, at standard temperature and pressure (25 °C, 760 mmHg), from 13.58 to 5.44 L/min. Gas composition is from 20 to 5000 ppm of SO_2, 5% O_2, and the balance N_2.

Since the reactor operates under a laminar flow regime, reactivity testing is performed at a S/Ca of 10 or greater to produce conditions that are differential with respect to SO_2. It has been verified experimentally that SO_2 starvation does not limit the calcium conversion observed. Variability in the reactor system is compensated for by replicating selected samples until the standard deviation falls to less than 10% of the mean.

Particle Size Analyses. Aerodynamic particle size analyses were performed by passing the particle-laden gases exiting the reactor through a heated Gelman inertial impactor (Gelman particle sizing stack sampler no. 4024-29). This particular impactor is used because of its ability to withstand temperatures up to 800 °C. The median diameter range of particles that can be classified is 0.44–7.55 μm in increments of seven trays. A preimpactor collects all particles larger than 11.9 μm.

Analyses. Specific surface area, porosity, and pore size distribution are measured by N_2 adsorption/desorption in a Micromeritics Digisorb 2600 autoanalyzer. Machine error is less than ±1%. Calcium utilization or conversion of reactor products is calculated after analyses for calcium by atomic absorption spectrophotometry and for sulfate by ion chromatography. Calcium utilization analyses have a precision of ±5%. No sulfur species other than sulfate have been detected.

Results and Discussion

In the course of studying the behavior of lignosulfonate-modified $Ca(OH)_2$, it has been noted that significant particle size reductions do not always accompany the observed increases in reactivity. In Figure 2, calcium conversion as a function of residence time and particle size is plotted for SM-$Ca(OH)_2$ and DH-$Ca(OH)_2$. It can be seen that for each particle size at each residence time the conversion of SM-$Ca(OH)_2$ exceeds that of DH-$Ca(OH)_2$. For each sorbent, the degree of conversion increases with decreasing particle size as expected. These data show convincingly that reduced particle size is not a prerequisite for enhanced reactivity in SM-$Ca(OH)_2$. In those applications where lignosulfonate does effect a size reduction, however, it would serve as an additional factor in enhancing reactivity with SO_2.

It has been suggested that the more rapid rate of dehydration of SM-$Ca(OH)_2$ may be part of the cause of its increased reactivity. More rapid dehydration would allow the sorbent more time in its oxide state to react with SO_2. The data in Figure 3 were produced to test this hypothesis. For SM-$Ca(OH)_2$ and DH-$Ca(OH)_2$, conversion is plotted against particle size for both the raw hydroxides and for CaO made from the hydroxides in an initial precalcination step. SM-$Ca(OH)_2$ was precalcined at 1000 °C for 1.5 s to produce SM-CaO having a specific surface area (S_A) of 24 m^2/g and a porosity (ϵ) of 31%. DH-$Ca(OH)_2$ was precalcined at 1000 °C for 0.6 s to produce DH-CaO with a $S_A = 22$ m^2/g and $\epsilon = 28\%$. If the dehydration step is decoupled from the sulfation reaction and the physical properties of the sorbents are kept very similar, the importance of the dehydration rate to the sulfation reaction can be determined. It can be seen from Figure 3 that SM-$Ca(OH)_2$ is more reactive than DH-$Ca(OH)_2$, as expected. It can also be seen that SM-CaO is more reactive with SO_2 than DH-CaO at all particle sizes. This demonstrates that the enhanced reactivity of SM-$Ca(OH)_2$ is not dependent on its more rapid rate of dehydration.

The lower conversion of the precalcines compared to the raw sorbents has been observed before and was assumed to be the result of a more advanced stage of sintering in the precalcine. Lange (1987) observed similar results and suggested that the raw sorbent is more reactive because of an unspecified effect caused by having SO_2 present during the calcination step. This is of particular interest because lignosulfonate is believed to retard sintering by delaying the solid-state diffusion mechanism that causes it. If the presence of SO_2 has a similar effect, the interaction or combined effect of the two species in modified sorbents may be important.

An earlier study by Kirchgessner and Jozewicz (1988) showed that SM-$Ca(OH)_2$ retained more of its porosity and surface area than DH-$Ca(OH)_2$ under similar reactor conditions. These observations were attributed to a lower rate of sintering in SM-$Ca(OH)_2$. Additional evidence for the difference in sintering behavior between SM-$Ca(OH)_2$ and DH-$Ca(OH)_2$ is offered in Figure 4. By plotting median pore diameter versus particle size, it can be seen that the larger median pore diameters caused by advanced sintering in small particles of DH-$Ca(OH)_2$ do not occur to the same extent in SM-$Ca(OH)_2$ where the sintering rate

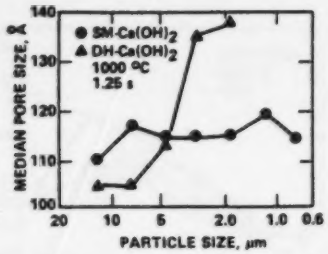

Figure 4. Median pore size as a function of particle size for SM-$Ca(OH)_2$ and DH-$Ca(OH)_2$.

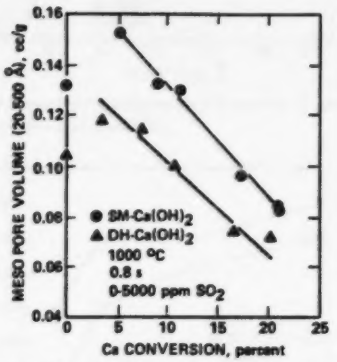

Figure 5. Changes in meso pore volume as a function of increasing calcium conversion for SM-$Ca(OH)_2$ and DH-$Ca(OH)_2$.

is reduced. With a reduction in particle size having been shown to be unnecessary and an enhanced dehydration rate ineffective in increasing the reactivity of the modified sorbent with SO_2, a reduced rate of sintering appears to be the most acceptable explanation.

In an effort to examine the effect of having SO_2 present during the calcination process, the change in intraparticle pore volume (20–500 Å) with increasing levels of calcium utilization was measured. To eliminate the effects of sintering, time and temperature were held constant at 0.8 s and 1000 °C, respectively. Different levels of conversion were affected by varying the SO_2 concentration from 0 to 5000 ppm. In Figure 5, the points on the vertical axis represent the pore volumes that the sorbents will sinter to, at this time and temperature, in the absence of SO_2. The next point to the right for each sorbent shows the conversion achieved (ca. 5%) and the resulting pore volume after exposure to 20 ppm of SO_2. Since the $CaSO_4$ product has approximately 3 times the volume of the original CaO reactant, one would expect an immediate reduction of porosity through the processes of pore filling and pore plugging. Instead, a higher pore volume results for both sorbents than occurred in the absence of SO_2. Although particle expansion during sulfation has been observed previously (Borgwardt and Harvey, 1972; Gullett and Bruce, 1987), it is not necessary to invoke expansion as an explanation for the results observed here. It would be sufficient for SO_2 to simply retard sintering of the CaO, perhaps by interfering with the solid-state diffusion-related exchanges of lattice vacancies and migrating reactant species at the pore face. The larger difference in pore volumes at low conversions than at higher conversions between SM-$Ca(OH)_2$ and DH-$Ca(OH)_2$ may suggest that, at low SO_2 levels, the effects of the lignosulfonate and SO_2 are combining to further retard sintering in the modified sorbent.

Figure 6 shows results from the same experiment as Figure 5 but plots specific surface area, instead of pore

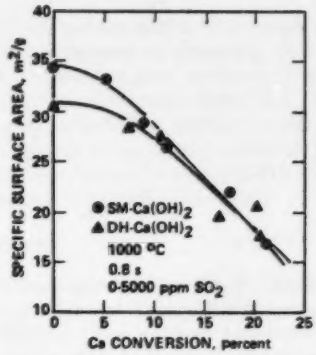

Figure 6. Changes in surface area as a function of increasing calcium conversion for SM-$Ca(OH)_2$ and DH-$Ca(OH)_2$.

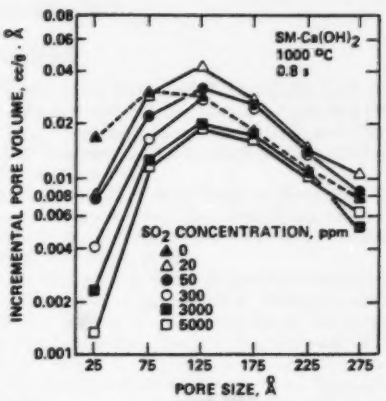

Figure 7. Incremental pore volume as a function of pore size and SO_2 concentration for SM-$Ca(OH)_2$.

volume, versus conversion. It can be seen that the rise in pore volume observed at low levels of conversion is not mirrored by a similar rise in surface area. The explanation would appear to lie in the range of pore sizes primarily affected by retardation in sintering versus those primarily affected by pore filling or plugging. The finest pores, which contribute much of the surface area, would be the first ones removed by sintering and the first ones to be plugged or filled by reaction product. Regardless of the ability of lignosulfonate and SO_2 to reduce sintering of pores in this range, the dominant effect is one of pore filling or plugging, and surface area is immediately lost. The effect of lignosulfonate alone to reduce sintering can be seen in the higher surface area of SM-$Ca(OH)_2$ in the absence of SO_2.

To determine if finer pores are preferentially filled or plugged, while larger pores are preserved through reduced sintering, incremental pore volume is plotted versus pore size as a function of SO_2 concentration. Figure 7 shows the results for SM-$Ca(OH)_2$, and Figure 8 shows the results for DH-$Ca(OH)_2$. In both figures it can be seen that, for all levels of SO_2 concentration, there is less incremental pore volume below 75 Å than in the unsulfated sample. In this size range, incremental pore volume also decreases consistently as SO_2 concentration increases, suggesting that pore plugging or filling is dominant. For pores between 75 and 275 Å, the ability of SO_2 to delay sintering can be observed. In the SM-$Ca(OH)_2$ shown in Figure 7, this effect holds for SO_2 concentrations up to 300 ppm. In the DH-$Ca(OH)_2$ on Figure 8, which lacks the effect of lignosulfonate, SO_2 concentrations up to 3000 ppm retain an effect. The lower incremental pore volumes in DH-$Ca(OH)_2$ than in SM-$Ca(OH)_2$ for all pore sizes are consistent

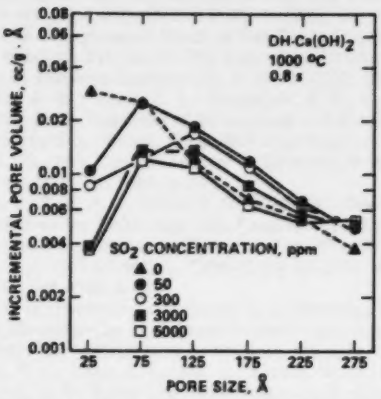

Figure 8. Incremental pore volume as a function of pore size and SO_2 concentration for DH-$Ca(OH)_2$.

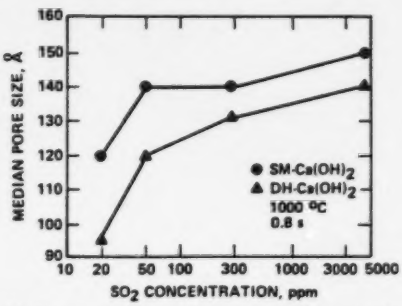

Figure 9. Median pore size as a function of SO_2 concentration for SM-$Ca(OH)_2$ and DH-$Ca(OH)_2$.

with the results reported previously (Kirchgessner and Jozewicz, 1988).

Figure 9 shows the result of fine pore plugging most clearly. Median pore size versus SO_2 concentration is shown for both sorbents. In both cases median pore size increases steadily with SO_2 concentration, indicating the plugging of the finer pores. SM-$Ca(OH)_2$ shows larger mean pore sizes than DH-$Ca(OH)_2$ for all SO_2 concentrations, reflecting its higher reactivity with SO_2. This is similar to the results in Figures 7 and 8 for the size range below 75 Å. In this range, for all comparable SO_2 concentrations, SM-$Ca(OH)_2$ had lower incremental pore volumes than DH-$Ca(OH)_2$, which also suggests more rapid plugging of finer pores in the modified sorbent.

Conclusions

The consistently high reactivity of modified hydroxides with SO_2 has been demonstrated. It does not appear that reduced particle size is a prerequisite to enhanced reactivity in SM-$Ca(OH)_2$, although in those applications where size reduction results, it will undoubtedly produce an additional benefit. Comparison of precalcined sorbents made from modified and unmodified hydroxides shows that the modified sorbent continues to be more reactive. This suggests that the previously observed higher rate of dehydration by the modified hydroxide is not an important mechanism in its enhanced reactivity with SO_2. The predominant effect of lignosulfonate modification appears to be a reduction in the rate of sintering in the reactive sorbent.

The presence of low SO_2 concentrations during calcination appears to affect the structure of sorbents favorably, allowing them to retain higher pore volumes than in the absence of SO_2. It is suggested that the deposition of calcium sulfate on pore surfaces may inhibit the exchange of the migrating CaO species with lattice vacancies. In the solid-state diffusion process of sintering, this exchange would normally occur along pore surfaces. This effect is most visible in the pore size range above 75 Å. Below this size, pore plugging and filling appear to predominate. There does not appear to be strong evidence for a reinforcing effect between lignosulfonate and SO_2 in retarding the rate of sintering in modified sorbents.

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Registry No. SO_2, 7440-09-7; $Ca(OH)_2$, 1305-62-0; calcium lignosulfonate, 8061-52-7.

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